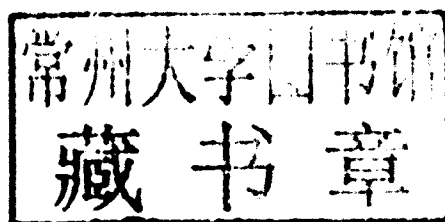PDL HANDBOOK SERIES

The Effect of Long Term Thermal Exposure on Plastics and Elastomers

Laurence W. McKeen

THE EFFECT OF LONG TERM THERMAL EXPOSURE ON PLASTICS AND ELASTOMERS

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Preface

This book is the eighth on the PDL series on plastics properties. It is a first edition and focuses on the effects long-term heat exposure has on the properties of plastics.

Plastics of mostly similar polymer types are grouped into 10 chapters. A brief explanation of the chemistry of the polymers used in the plastic compounds or formulations is discussed at the start of each plastic section. This is generally consistent with the other seven books in this particular series. This book is a logical extension to the *Effect of Temperature and Other Factors on Plastics and Elastomers* (*2nd Edition*) published by William Andrew Publishing/Plastics Design Library in 2008 which focuses on the short-term effect of temperature on the properties of plastics.

An extensive introduction covers the first three chapters. The initial chapter covers polymer chemistry, plastics, and composition and how it relates to various general plastics properties. The second chapter focuses on the main subject of this book, that of the effect of heat on plastics. It gives an overview of the chemistry of thermodegradation and thermooxidation. There is a section on heat stabilizers that includes chemical structures and mode of operation. It also covers methods used to heat age plastics, particularly those that are accelerated in nature. The generation of thermal endurance curves are discussed and extension of those to temperatures not tested. The third chapter focuses on physical, mechanical, thermal, and electrical properties of plastics. Many plastic properties are discussed including how the properties are measured and data is presented.

Chapters 4 through 11 are a databank that serves as an evaluation of the performance of hundreds of plastic materials after long-term exposure to heat. Each of these chapters starts with a brief outline of the chemistry of the polymer in that section. There are hundreds of uniform graphs and tables for more than 70 generic families of plastics used to make plastics contained in these chapters.

The data in each chapter is generally organized with polymer chemistry, thermooxidation chemistry, a manufacturer and trade name list, an applications and end uses list followed by the data. Numerous references are included.

I am especially appreciative of the confidence and support of my Plastics Design Library series editor and friend Sina Ebnesajjad. I would not have been given the opportunity to do this work had it not been for the support of Mathew Deans, Senior Publisher at Elsevier. His staff at Elsevier is knowledgeable and easy to work with. My wife, Linda, has been particularly supportive through the long hours of writing and research from my home office.

Laurence W. McKeen
2013

Contents

1 Introduction to Plastics and Polymers

The basic component of plastic and elastomer materials is polymer. The word polymer is derived from the Greek term for "many parts." Polymers are large molecules comprised of many repeat units, called monomers that have been chemically bonded into long chains. Since World War II, the chemical industry has developed a large quantity of synthetic polymers to satisfy the materials need for a diverse range of products, including paints, coatings, fibers, films, elastomers, and structural plastics. Literally thousands of materials can be called "plastics," although the term today is typically reserved for polymeric materials, excluding fibers, which can be molded or formed into solid or semisolid objects. As of the beginning of 2013, IDES The Plastics Web® (http://www.ides.com) listed over 86,000 different grades of plastic from over 900 suppliers.

There are three introductory chapters to this book. The first chapter is a review of polymer chemistry and plastic formulation. It lays the basis for the discussion on thermal degradation, property measurement, and all the data chapters. The second chapter is a review of thermal degradation of polymers. This includes the various ways to expose test plaques. The physical and chemical processes involved with long-term exposure are explained. The third chapter is on plastic properties, what they are and how they are measured. First discussed are the physical properties. Second are the mechanical properties such as tensile strength, elongation, modulus, and tear resistance. Third are thermal properties such as melting point, glass transition temperature, and melt index which affect use, production, and processing of films.

The chapters that follow are the data chapters. Each chapter covers plastics that generally fall into particular types based on the chemistry of the polymer. Each of these chapters reviews the chemical structures of the polymers used to make the plastics.

The subject of this first chapter includes polymerization chemistry and the different types of polymers and how they can differ from each other. Since plastics are rarely "neat", reinforcement, fillers, and additives are reviewed. A basic understanding of plastic and polymer chemistry will make the discussion of properties of specific films easier to understand and it also provides a basis for the introductions of the plastic families in later chapters. This chapter is taken from *The Effect of Temperature and Other Factors on Plastics* [1] and *Permeability Properties of Plastics and Elastomers* [2], but it has been rewritten, expanded, and refocused on polymers as they relate plastics that may be exposed to various heating processes.

1.1 Polymerization

Polymerization is the process of chemically bonding monomer building blocks to form large molecules. Commercial polymer molecules are usually thousands of repeat units long. Polymerization can proceed by one of several methods. The two most common methods are called addition and condensation polymerization.

1.1.1 Addition Polymerization

In *addition polymerization* (sometimes called chain-growth polymerization), a chain reaction adds new monomer units to the growing polymer molecule one at a time through double or triple bonds in the monomer. The polymerization process takes place in three distinct steps:

1. *Chain initiation*: Usually by means of an initiator which starts the polymerization process. The reactive initiation molecule can be a radical (free radical polymerization), cation (cationic polymerization), anion (anionic polymerization), and/or organometallic complex (coordination polymerization).

2. *Chain propagation*: A monomer adds onto chain and each new monomer unit creates an active site for the next attachment. The net result is shown in Figure 1.1.

3. *Chain termination*: The radical, cation, or anion is "neutralized" stopping the chain propagation.
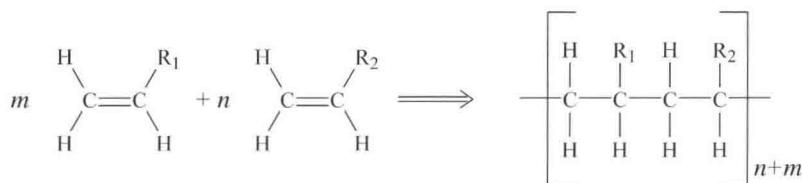
Figure 1.1 Addition polymerization.
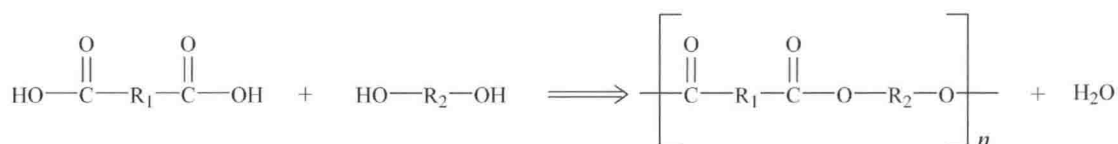
Figure 1.2 Condensation polymerization.

Many of the plastics discussed in later chapters of this book are formed in this manner. Some of the plastics made by addition polymerization include polyethylene, polyvinyl chloride, acrylics, polystyrene, and polyoxymethylene (acetal).

1.1.2 Condensation Polymerization

The other common method is *condensation polymerization* (also called *step-growth polymerization*) in which the reaction between the monomer units and the growing polymer chain end group releases a small molecule, often water as shown in Figure 1.2. The monomers in this case have two reactive groups. This reversible reaction will reach equilibrium and halt unless this small molecular by-product is removed. Polyesters and polyamides are among the plastics made by this process.

Understanding the polymerization process used to make a particular plastic gives insight into the nature of the plastic. For example, plastics made via condensation polymerization, in which water is released, can degrade when exposed to water at high temperature. Polyesters such as polyethylene terephthalate (PET) can degrade by a process called hydrolysis when exposed to acidic, basic, or even some neutral environments severing the polymer chains. As a result the polymer's properties are degraded.

1.2 Copolymers

A copolymer is a polymer formed when two (or more) different types of monomer are linked in the same polymer chain, as opposed to a homopolymer where only one monomer is used. If exactly three monomers are used, it is called a terpolymer.

Monomers are only occasionally symmetric; the molecular arrangement is the same no matter which end of the monomer molecule you are looking at. The arrangement of the monomers in a copolymer can be head-to-tail, head-to-head, or tail-to-tail. Since a copolymer consists of at least two types of repeating units, copolymers can be classified based on how these units are arranged along the chain. These classifications include the following:

- Alternating copolymer
- Random copolymer (statistical copolymer)
- Block copolymer
- Graft copolymer.

In the following examples A and B are different monomers. Keep in mind the A and B do not have to be present in a one to one ratio. When the two monomers are arranged in an alternating fashion, the polymer is called, of course, an alternating copolymer.

–A–B–A–B–A–B–A–B–A–B–A–B–A–B–A–B–A–B–

Alternating copolymer

In a random copolymer, the two monomers may link in any order.

–A –A–B–A–B–B–A–B–A–A–B–B–B–A–B–A–A–

Random copolymer

In a block copolymer, all of one type of monomer is grouped together, and all of the second monomer are grouped together. A block copolymer can be thought of as two homopolymers joined together at the ends.

–A–A–A–A–A–A–A–A–A–B–B–B–B–B–B–B–B–B–
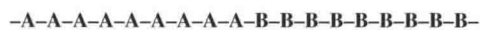
Block copolymer

A polymer that consists of large grouped blocks of each of the monomers is also considered a block copolymer.

–A–A–A–A–A–A–B–B–B– B–B–B–A–A–A–A–A–
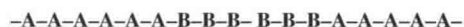
Block copolymer

When chains of a polymer made of monomer B are connected onto a polymer chain of monomer A we have a graft copolymer.
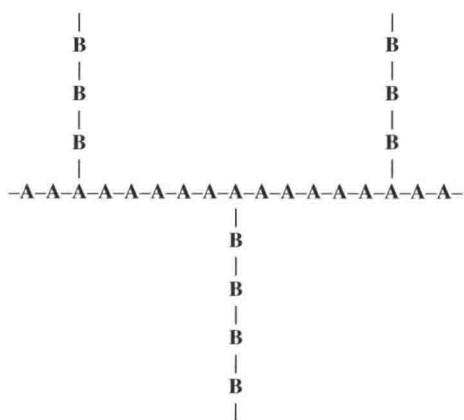
Branched/grafted Copolymer

High-impact polystyrene, or HIPS, is a graft copolymer. It is a polystyrene backbone with chains of polybutadiene grafted onto the backbone. The polystyrene gives the material strength, but the rubbery polybutadiene chains give it resilience to make it less brittle.

1.3 Linear, Branched, and Crosslinked Polymers

Some polymers are linear, a long chain of connected monomers. Polyethylene, polyvinyl chloride, Nylon 66, and polymethyl methacrylate are some linear commercial examples found in this book. Branched polymers can be visualized as a linear
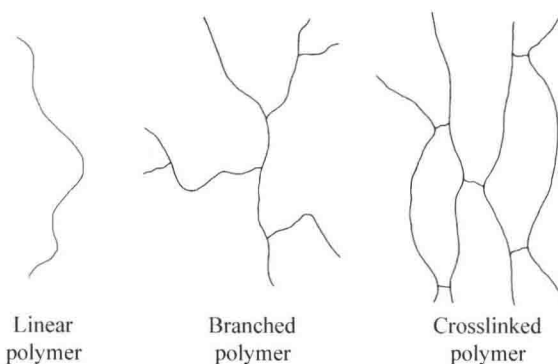
Figure 1.3 Linear, branched, and crosslinked polymers.

polymer with side chains of the same polymer attached to the main chain. While the branches may in turn be branched, they do not connect to another polymer chain. The ends of the branches are not connected to anything. Special types of branched polymers include star polymers, comb polymers, brush polymers, dendronized polymers [3], ladders, and dendrimers. Crosslinked polymer, sometimes called network polymer, is one in which different chains are connected. Essentially the branches are connected to different polymer chains on the ends. These three polymer structures are shown in Figure 1.3.

1.4 Polarity

A molecule is two or more atoms joined by a covalent bond. Basically the positively charged atom nuclei share the negatively charged electrons. However, if the atoms are different they may not share the electrons equally. The electrons will be denser around one of the atoms. This would make that end more negatively charged than the other end and that creates a negative pole and a positive pole (a *dipole*), and such a bond is said to be a *polar bond* and the molecule is polar and has a *dipole moment*. A measure of how much an atom attracts electrons is *electronegativity*. The electronegativity of common atoms in the polymers follows:

$$F > O > Cl \text{ and } N > Br > C \text{ and } H.$$

The polarity of a molecule affects the attraction between molecular chains, which affects the structure of the polymer and the attraction of polar

Table 1.1 Dipole Moments in Some Small Molecules

Molecule	Dipole Moment	Molecule	Dipole Moment	Molecule	Dipole Moment
H_2	0	HF	1.75	CH_4	0.0
O_2	0	H_2O	1.84	CH_3Cl	1.86
N_2	0	NH_3	1.46	CCl_4	0
Cl_2	0	NF_3	0.24	CO_2	0
Br_2	0	BF_3	0		

molecules, so one would expect polarity to affect solubility which affects permeability.

How does one predict molecular polarity? When there are no polar bonds in a molecule, there is no permanent charge difference between one part of the molecule and another so the molecule is nonpolar. For example, the Cl_2 molecule has no polar bonds because the electron charge is identical on both atoms. It is therefore a nonpolar molecule. The C—C and C—H bonds in hydrocarbon molecules, such as ethane, C_2H_6, are not significantly polar, so hydrocarbons are nonpolar molecular substances and hydrocarbon polymers like polyethylene or polypropylene are nonpolar also.

A molecule can possess polar bonds and still be nonpolar, however. If the polar bonds are evenly (or symmetrically) distributed, the bond dipoles cancel and do not create a molecular dipole. For example, the three bonds in a molecule of CCl_4 are significantly polar, but they are symmetrically arranged around the central carbon atom. No side of the molecule has more negative or positive charge than another side, and so the molecule is nonpolar (Table 1.1).

Generally polar polymers are more permeable to water than nonpolar polymers. Figure 1.4 shows a qualitative ranking of some polymers polarities.

1.5 Unsaturation

Up to this point in the discussion of polymer chemistry, the atom to atom structure has not been discussed. The covalent bonds between atoms in a polymer can be single, double, triple bonds, or even rings. The presence of bonds higher than single bonds generally makes the polymer molecule stiffer and reduces freedom of rotation along the polymer chain and that can affect its properties. It is easier to discuss molecules first and then extend that

High polarity   Nylon 6/6
Nylon 6
Polyethylene terephthalate (PET)
Cellulose acetate
Nitrile rubber (NBR) (50% acrylonitrile)
Polyurethane
Nitrocellulose
Epoxy
Polycarbonate (PC)
Polymethyl methacrylate (PMMA)
Polyvinyl acetate
Nitrile rubber (NBR) (30% acrylonitrile)
Acrylate elastomers
Polyvinyl butyral
Polyepichlorohydrin
Cellulose acetate butyrate
Polystyrene
Polyvinyl alcohol
Polychloroprene
Polyethylene
Nitrile rubber (NBR) (20% acrylonitrile)
Chlorinated polyethylene
Styrene–butadiene rubber (SBR)
Polybutadiene
Natural rubber
Halogenated butyl
Polypropylene
Ethylene propylene diene monomer rubber (EPDM)
Butyl rubber
Perfluorinated polymers
Low polarity   Silicone

Figure 1.4 Qualitative ranking of polymer polarities.

discussion to polymers. Saturated molecules only contain single bonds with no rings.

Often when talking about molecular unsaturation, the *degree of unsaturation* is noted. Calculation of the degree of unsaturation (DoU), if the molecular formula is given, it uses the formula (Eq. (1.1)):

$$DoU = \frac{2C + 2 + N - X - H}{2} \qquad (1.1)$$

- C = number of carbons
- N = number of nitrogens

- X = number of halogens (F, Cl, Br, I)
- H = number of hydrogens
- Oxygen and sulfur are not included in the formula because saturation is unaffected by these elements.

Examples:

$$\text{Ethylene: } C_2H_4 \ \text{DoU} = \frac{2C + 2 + N - X - H}{2}$$
$$= \frac{2 \times 2 + 2 + 0 - 0 - 4}{2} = 1$$
(1.2)

$$\text{Benzene: } C_6H_6 \ \text{DoU} = \frac{2C + 2 + N - X - H}{2}$$
$$= \frac{2 \times 6 + 2 + 0 - 0 - 6}{2} = 4$$
(1.3)

When polymers are used the formula shown is often the repeating unit (Figure 1.5). This will often have two bonds that are shown to which the repeating unit is supposed to attach. If applying a DoU formula to the repeating unit one would remove the " + 2" in the formula.

Examples:

$$\text{Polyethylene(PE): } - (CH_2 - CH_2)_n - \text{DoU}$$
$$= \frac{2C + N - X - H}{2} = \frac{2 \times 2 + 0 - 0 - 4}{2} = 0$$
(1.4)

$$\text{Polyphenylene sulfide(PPS): } - (C_6H_4 - S)_n - \text{DoU}$$
$$= \frac{2C + N - X - H}{2} = \frac{2 \times 6 + 0 - 0 - 4}{2} = 4$$
(1.5)

1.6 Steric Hindrance

As described earlier in this chapter, polymers are long chains of atoms linked together. They may be flexible and bendable. To explain this one may visualize them as ball-and-stick model. In chemistry, the ball-and-stick model is a molecular model of a chemical substance which aims to display both the three-dimensional position of the atoms and the bonds between them. The atoms are typically
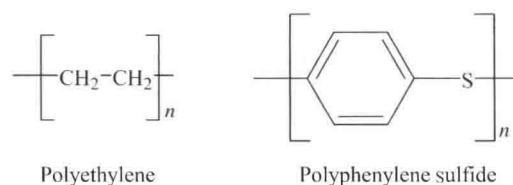
Figure 1.5 Example polymer structures.
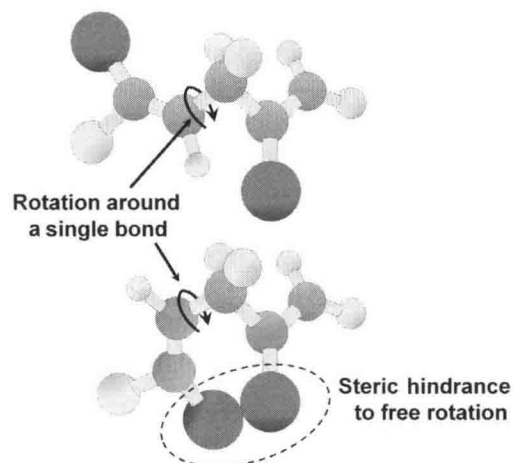
Figure 1.6 Steric hindrance shown with a ball-and-stick molecular model.

represented by spheres, connected by rods which represent the bonds. Double and triple bonds are usually represented by two or three curved rods, respectively. The chemical element of each atom is often indicated by the sphere's color and size. The top of Figure 1.6 shows a drawing of a ball-and-stick model of a molecule. Figure 1.6 also indicates that there is free rotation around the single bonds. If there was a double or triple bond there would not be any rotation possible around those bonds. Similarly, ring structures, while they might flex a little bit, inhibit rotation. In some cases such as shown in the bottom of Figure 1.6 large atoms or bulky side groups might bump into each other as the molecule rotates around single bonds. This is called *sterically hindered* or *steric hindrance*. Hindered or inhibited rotation stiffens the polymer molecule and dramatically affects its physical properties.

1.7 Isomers

Isomers (from Greek isomerès; isos = "equal", méros = "part") are compounds with the same

molecular formula but a different arrangement of the atoms in space. There are many kinds of isomers and the properties can differ widely or almost not at all.

1.7.1 Structural Isomers

Structural isomers have the atoms arranged in a completely different order as shown in Figure 1.7. Here both the polymer repeating groups have the same formula, $-C_4H_8-$, but the atoms are arranged differently. The properties of structural isomers may be very different from each other.

Often the repeating group in a polymer is exactly the same formula, but the repeating group is flipped over as shown in Figure 1.8. If one views the repeating group as having a head and a tail then the different ways to connect neighboring repeating units is head—tail, head—head, and tail—tail.

1.7.2 Geometric Isomers

When there is a carbon—carbon double bond is a molecule there might also be two ways to arrange the groups attached to the double bonds. This is best seen in side-by-side structures such as shown in Figure 1.9.

These are called *geometric isomers* that owe their existence to hindered rotation about double bonds. If the substituents are on the same side of the double bond, then the isomer is referred to as *cis*- (Latin: on this side). If the substituents are on
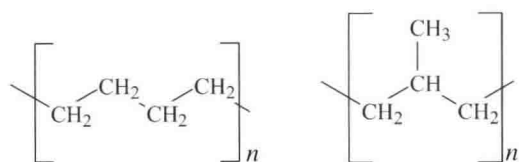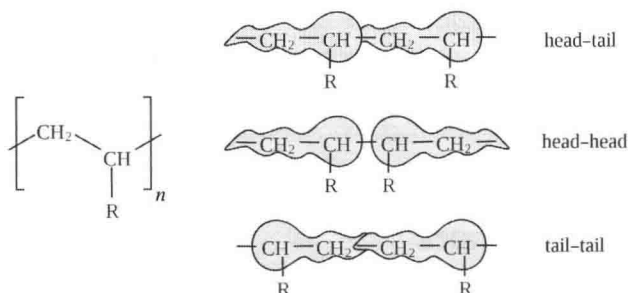
the opposite side of the double bond are referred to as *trans*- (Latin: across).

1.7.3 Stereoisomers— Syndiotactic, Isotactic, Atactic

Stereoisomerism occurs when two or more molecules have identical molecular formula and the same structural formula (i.e., the atoms are arranged in the same order). However, they differ in their 2D or 3D spatial arrangements of their bonds—which mean different spatial arrangement of the atoms—even though they are bonded in the same order. This may best be understood by example.

Polypropylenes have the same simplified structural polymer formula of polypropene as shown in Figure 1.10.

However, there are subtle differences in the ways to draw this structure. Figure 1.11 shows a longer structure of polypropene, one that also shows some 3D structure. This structure shows how some bonds (the dotted lines) are behind the plane of the paper and others stick out of the paper (the ones on the ends of the little triangular wedges). In this structure, some of the methyl ($-CH_3$) groups are above the paper plane and others are behind the paper plane. This is called *atactic* polypropene.

Atactic polypropene has at random about 50% of hydrogen/methyl groups in front/back of C—C—C chain viewing plane. This form of polypropene is amorphous (noncrystalline, discussed in Section 1.9.3)
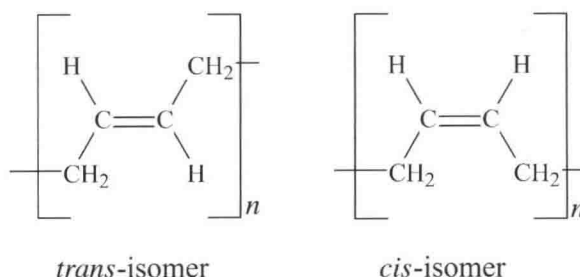
Figure 1.7 Structural isomers.

Figure 1.8 Head-to-tail Isomers [4].

trans-isomer   *cis*-isomer
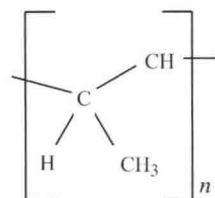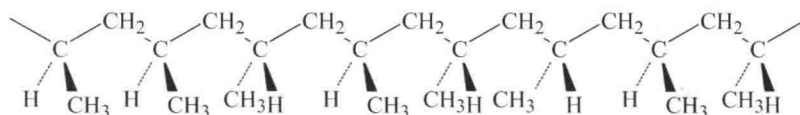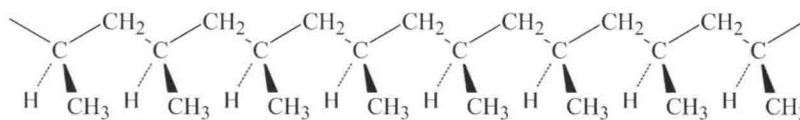
Figure 1.9 *Cis*- and *trans*-isomers.
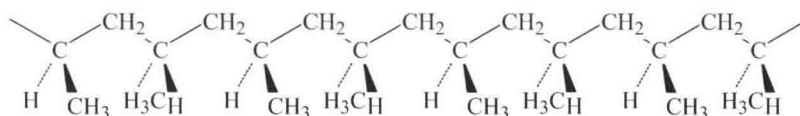
Figure 1.10 The structure of polypropene.

Figure 1.11 The structure of atactic polypropene.

Figure 1.12 The structure of isotactic polypropene.

Figure 1.13 The structure of syndiotactic polypropene.

and has an irregular structure due to the random arrangement of the methyl groups attached to the main carbon–carbon chain. It tends to be softer and more flexible than the other forms (described below) and is used for roofing materials, sealants and other weatherproof coatings.

Isotactic polypropene has all of the methyl groups in front of C–C–C chain viewing plane and all of the Hs at back as shown in Figure 1.12. This stereoregular structure maximizes the molecule–molecule contact and so increasing the intermolecular forces compared to the atactic form. This regular structure is much stronger (than the atactic form above) and is used in sheet and film form for packaging and carpet fibers.

Syndiotactic polypropene has a regular alternation of 50% of hydrogen/methyl groups in front/back of –C–C–C–chain viewing plane as shown in Figure 1.13. Its properties are similar to isotactic polypropene rather than the atactic form, i.e., the regular polymer structure produces stronger intermolecular forces and a more crystalline form than the atactic polypropene.

1.8 Inter- and Intramolecular Attractions in Polymers

The attractive forces between different polymer chains or segments within polymer chains play a large part in determining a polymer's properties. As mentioned in Section 1.4, atoms can have polarity or dipole moments. Since negative charges are attracted to the opposite positive charges and repelled by like charges it is possible to generate attractions that lead to certain structures.

1.8.1 Hydrogen Bonding

One of the strongest dipole interactions is the attraction of some oxygen atoms to hydrogen atoms even though they are covalently bonded to other atoms. This is called hydrogen bonding and a schematic of it is shown in Figure 1.14. The N–H bond provides a dipole when the hydrogen has a slightly positive charge and the nitrogen has a slightly negative charge. The carbonyl group, the C=O, likewise is a dipole, where the oxygen has the slight negative charge and the carbon is slightly positive. When polymer chains line up these *hydrogen bonds* are formed (indicated by the wide gray bars in the figure), bonds that are far weaker than the covalent bonds but bonds of significant strength nonetheless.

Other side groups on the chain polymer can lend the polymer to hydrogen bonding between its own chains. These stronger forces typically result in higher tensile strength and higher crystalline melting points. Polyesters have dipole–dipole bonding between the oxygen atoms in C=O groups and the hydrogen atoms in H–C groups. Dipole bonding is not as strong as hydrogen bonding.